

# Amide and Combined Amide/Borohydride Investigations

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**Savannah River National Laboratory**

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# Overview

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## Timeline

- **Start: 10/1/05**
- **End: 9/30/10**
- **Percent complete: 83%**

## Budget

- **Funding for FY09**
  - **\$400K**
- **Funding for FY10**
  - **\$350K**

## Barriers Addressed

- A. System Weight and Volume**
- E. Charging/Discharging Rate**
- P. Understanding Chemisorption**

## Partners

- **Z. Fang – U. of Utah**
- **H. zurLoye – U. of South Carolina**  
**D. Bugaris – U. of South Carolina**
- **E. Ronnebro – PNNL**  
**T. Autrey – PNNL**
- **Hydrogen Storage Engineering CoE**
- **D. Chandra – U. of Nevada-Reno**



# Relevance – Objectives and Motivation

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## Task I - LiMgN

- Perform isothermal/isobaric hydrogenation and dehydrogenation experiments to analyze the effect of **composition** on the **kinetics** of the LiMgN system.
- Formulate an outline of discharge and charge conditions to **prepare a hydrogen storage system** based on the kinetics.
- Prepare a **database** for use by the Hydrogen Storage Engineering Center of Excellence (**HSECoE**) to assess the utility of LiMgN in a **prototype system**.

## Task II - $M_1M_2(BH_4)_x(NH_2)_y$

- Perform an empirical study of **high hydrogen content** bimetallic **mixed borohydride/amide** systems of the form:  $M_1M_2(BH_4)_x(NH_2)_y$ . These systems include  $Mg(BH_4)_2/LiNH_2$ ,  $Mg(NH_2)_2/LiBH_4$ , and  $Ca(NH_2)_2/LiBH_4$ .
- Investigate the **addition of  $NH_3BH_3$  to  $Ca(BH_4)_2$  and  $LiNH_2$**  as a potential high hydrogen containing mixture.

## Relevance –

# LiMgN as a Hydrogen Storage Material



- Identified using DFT calculations as potentially reversible with a theoretical H<sub>2</sub> gravimetric storage capacity of **8.2 wt%** (Alapati *et al.*, *Phys. Chem. Chem. Physics*. 9 (2007) 1438)
  - Experimentally **8.1 wt%** was observed by Lu *et al.* under moderate temperature (160°C to 220°C) using TGA after **jar rolling** for 12 to 24 hours (Lu *et al.*, *J. Phys. Chem. C* 111 (2007) 12129)

- The reversible hydrogen absorption reaction involved



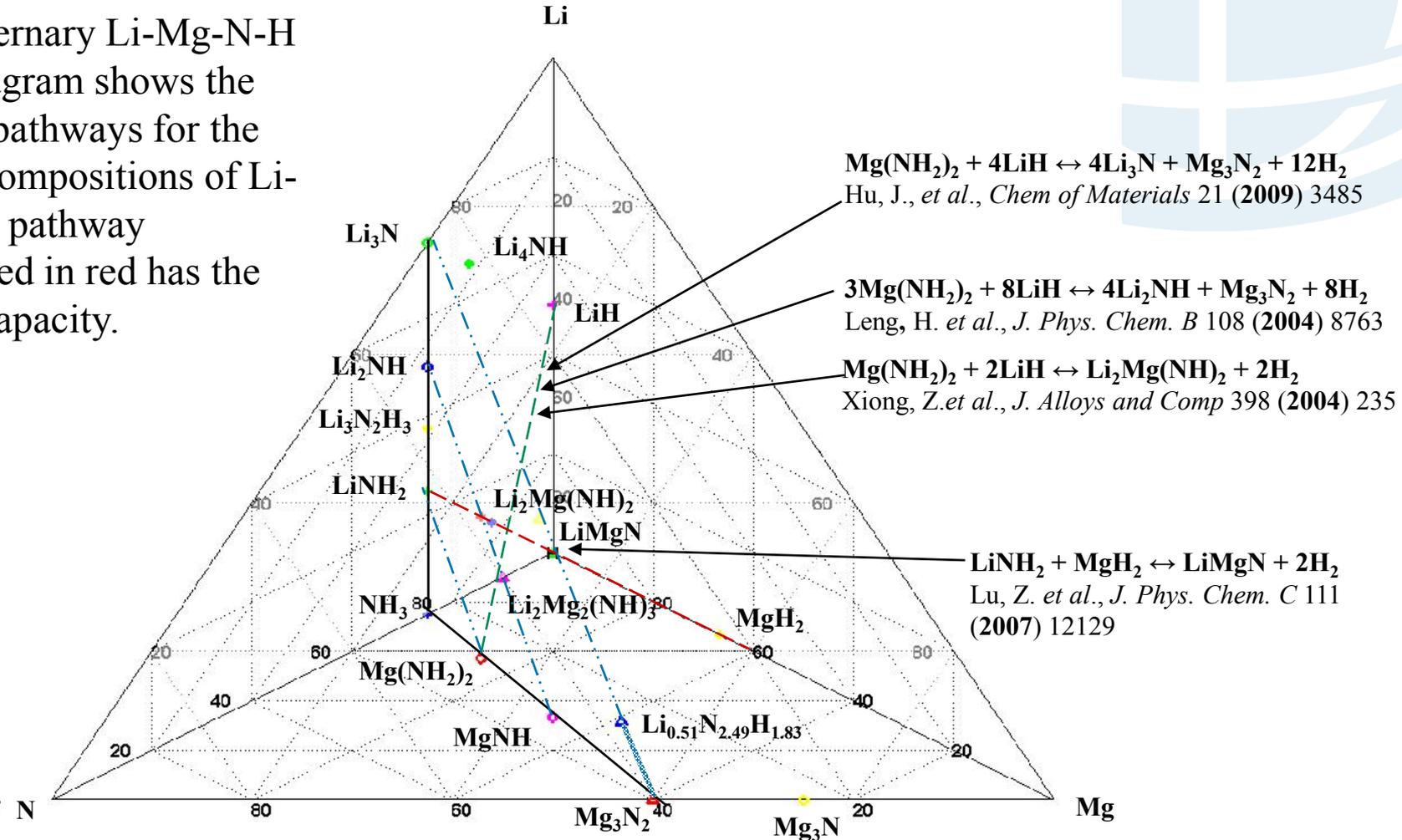
- **8 wt%** observed experimentally at 160°C and 140 bar in pressure vessel
- Dehydrogenation is proposed to proceed through an intermediate step



- Accelerated reversibility has been observed using 4 wt% TiCl<sub>3</sub> dopant (Lu *et al.*, *J. Phys. Chem. C* 111 (2007) 12129)
- **Planetary milling** for **36 hours** resulted in 6.1 wt% lost by 390°C, the formation of Li<sub>2</sub>MgN<sub>2</sub>H<sub>2</sub>, a  $\Delta H_{\text{rxn}} = 45.9 \text{ kJ/molH}_2$  and a reversible capacity of **2.5 wt%** at 210°C/101 bar pressure (Liu *et al.*, *Chem. Mater.* 20 (2008) 3521)

# Approach – Li-Mg-N-H Quaternary Phase Diagram

The quaternary Li-Mg-N-H phase diagram shows the reaction pathways for the various compositions of Li-Mg. The pathway highlighted in red has the highest capacity.



# Approach – LiMgN Experimental Plan

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- Perform isothermal and isobaric kinetic studies under controlled reaction conditions
  - Explore effect of catalysts composition – Li:Mg: $M_{tr}$ 
    - $M_{tr} = TiCl_3, VCl_3, TiN, NiCl_2$  and  $ScCl_3$  with composition = 1.5 mol%
- XRD analysis performed on as-milled material and after hydrogenation/dehydrogenation cycles
- TGA-RGA to determine gas composition during dehydrogenation
- **Deliverable**: Experimental data necessary to determine isothermal kinetics, characterize the proposed reaction for hydrogenation and dehydrogenation and database for use by HSECoE to assess the utility of LiMgN in a prototype system

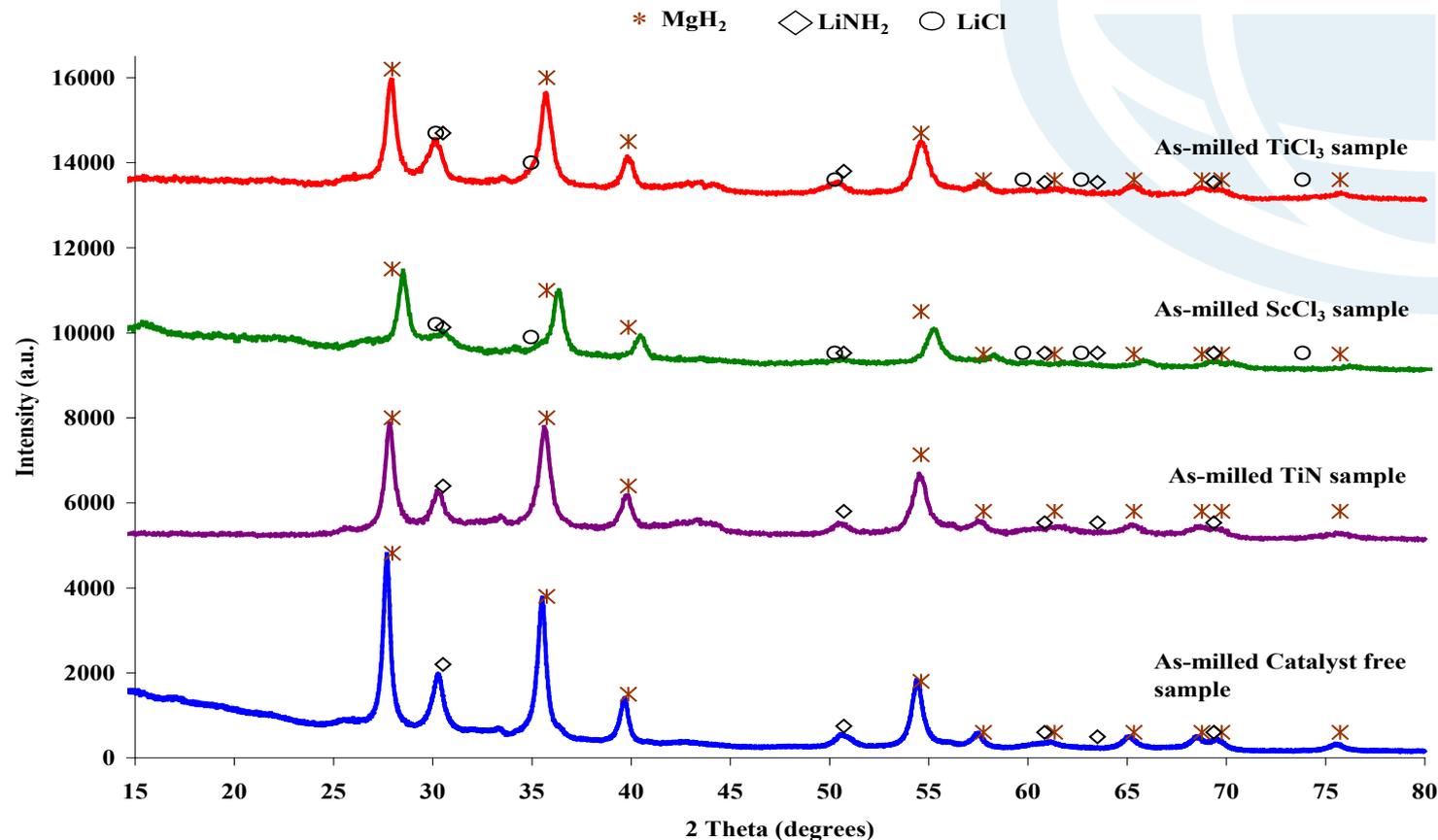
# Approach –

## Material Synthesis and Experimental Procedure

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- **Synthesis**
  - Starting materials include  $\text{LiNH}_2$  or  $\text{LiH}$ ,  $\text{MgH}_2$  and/or  $\text{Mg}(\text{NH}_2)_2$  and catalysts
  - All materials prepared using Fritsch mill rotational or jar roll milling techniques
  - FM for 2.5 hours at 500 rpm with rotational direction reversed every 30 minutes
  - Standard discharge condition:  $260^\circ\text{C}/1 \text{ bar}/6 \text{ hrs}$
  - Standard charge condition:  $180^\circ\text{C}/100 \text{ bar}/6 \text{ hrs}$
- **Discharge Procedure**
  - Reactor placed under high pressure ( $\sim 110 \text{ bar}$ ) and heated to desired temperature
  - Manifold controlled so that when the reactor is released to the reservoir, the nominal backpressure is equal to 1 bar
- **Charge Procedure**
  - Reactor placed under active vacuum and heated to desired temperature
  - Reservoir is pressurized to desired pressure and released to the reactor
- **TGA-RGA Procedure**
  - Heating rate at  $5^\circ\text{C}/\text{min}$  from RT to  $315^\circ\text{C}$
  - Looked at mass 2 ( $\text{H}_2$ ), 16 ( $\text{NH}_2^-$ ), 17 ( $\text{NH}_3/\text{OH}$ ) and 18 ( $\text{H}_2\text{O}$ ) in RGA

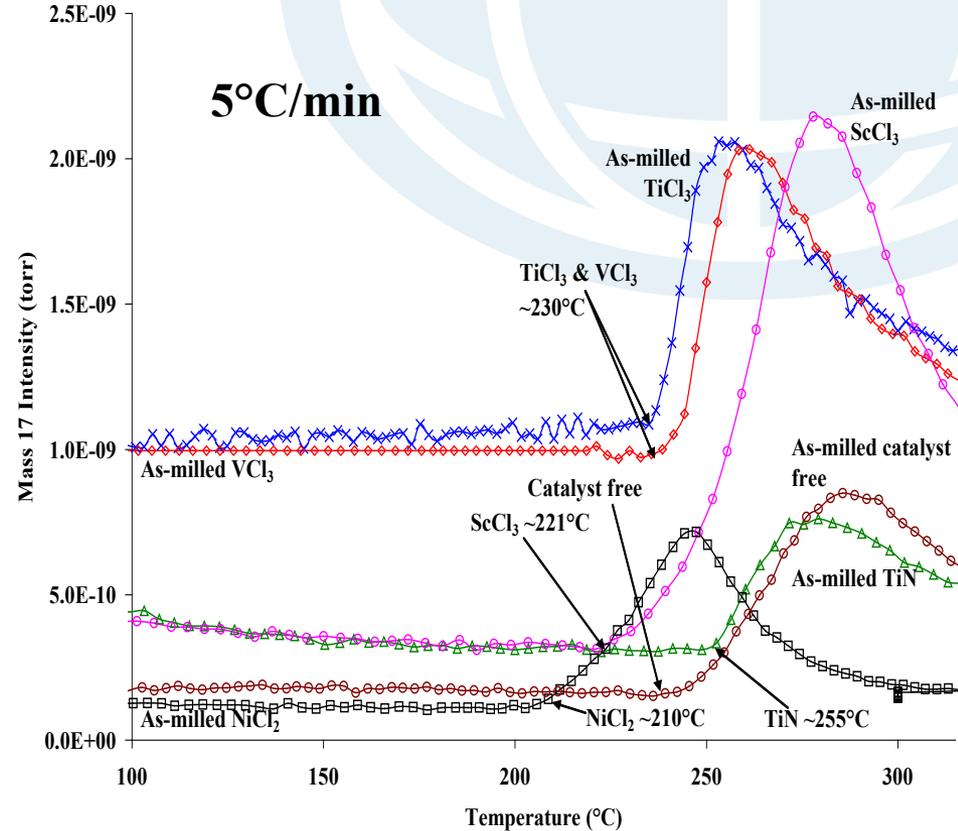
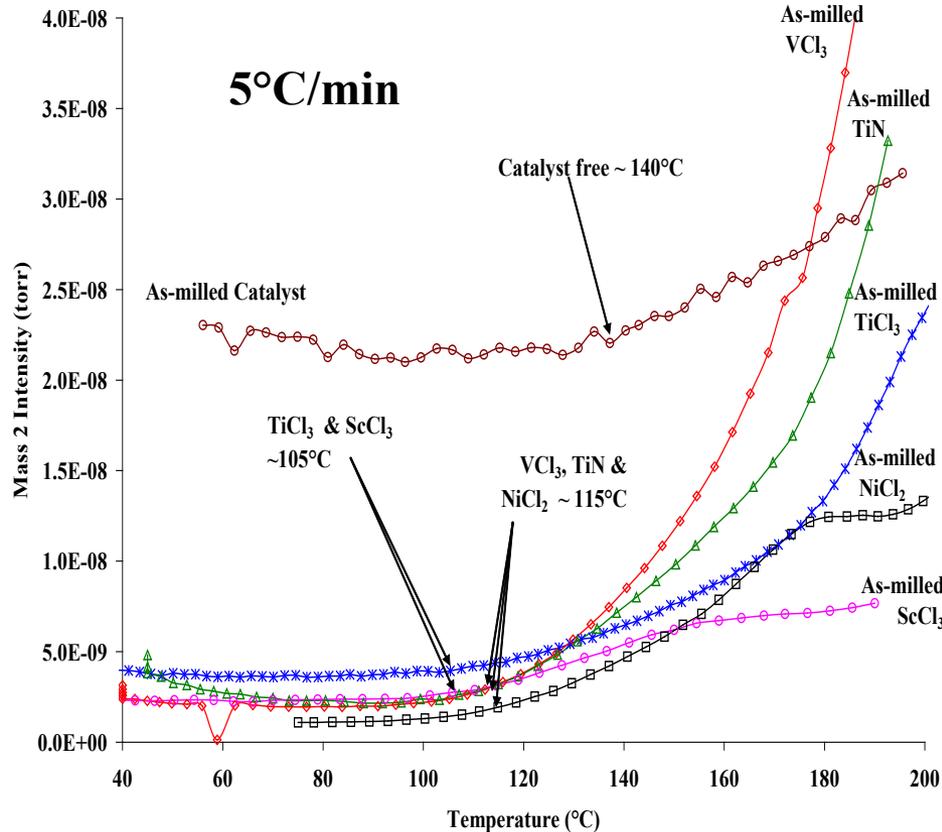
# Technical Accomplishments and Progress – XRD Analysis of As-milled 1:1 LiNH<sub>2</sub>:MgH<sub>2</sub> w/w/o catalyst



**MgH<sub>2</sub> and LiNH<sub>2</sub> patterns identified; however, LiCl also identified for halide catalysts**

- No indication of decomposition of TiN resulting from milling
- Metathesis reaction going on which produces LiCl in samples (ball-milling may provide enough energy to initiate the reaction) [observed by: Parkin *et al.*, *J. Mater. Chem.* **5**, (1995) 909.]

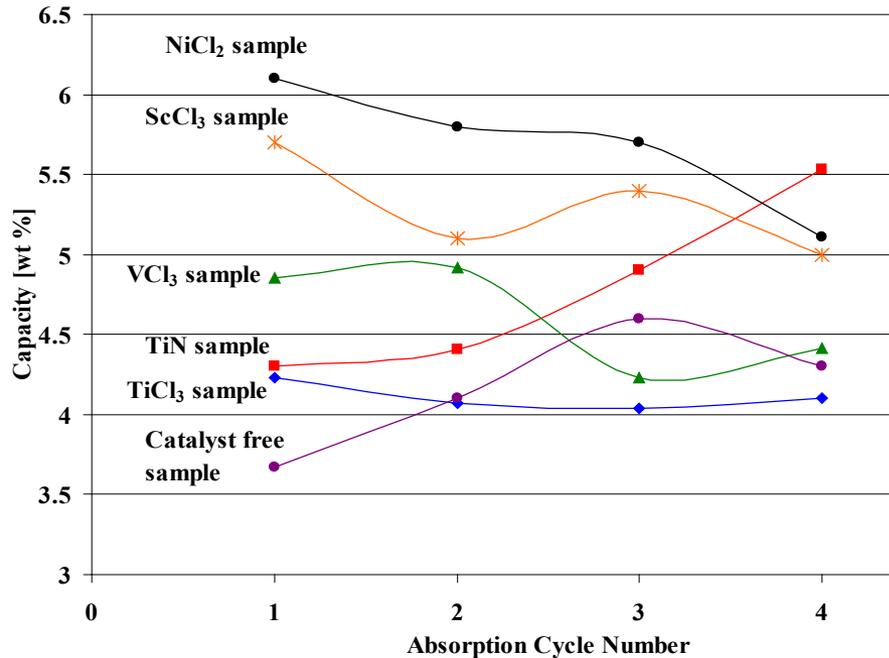
# Technical Accomplishments and Progress – RGA results of As-milled 1:1 LiNH<sub>2</sub>:MgH<sub>2</sub> w/w/o catalyst



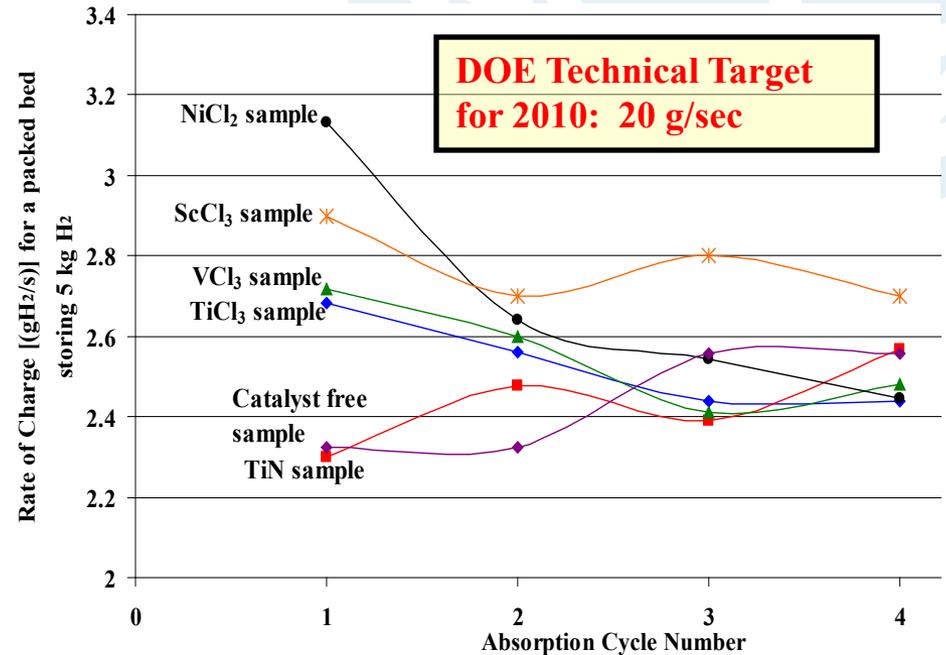
- All catalysts reduce 1<sup>st</sup> cycle hydrogen desorption temperature by 25 - 35°C
- Metathesis reaction between LiNH<sub>2</sub> and M<sub>tr</sub>Cl<sub>3</sub> promotes ammonia release
- Only TiN increased the temperature of initial ammonia release by 15°C

# Technical Accomplishments and Progress – Average Rate of Hydrogen Charge [gH<sub>2</sub>/s]

Hydrogen Capacity over four absorption cycles at 180 C under 100 bar for 6 hours



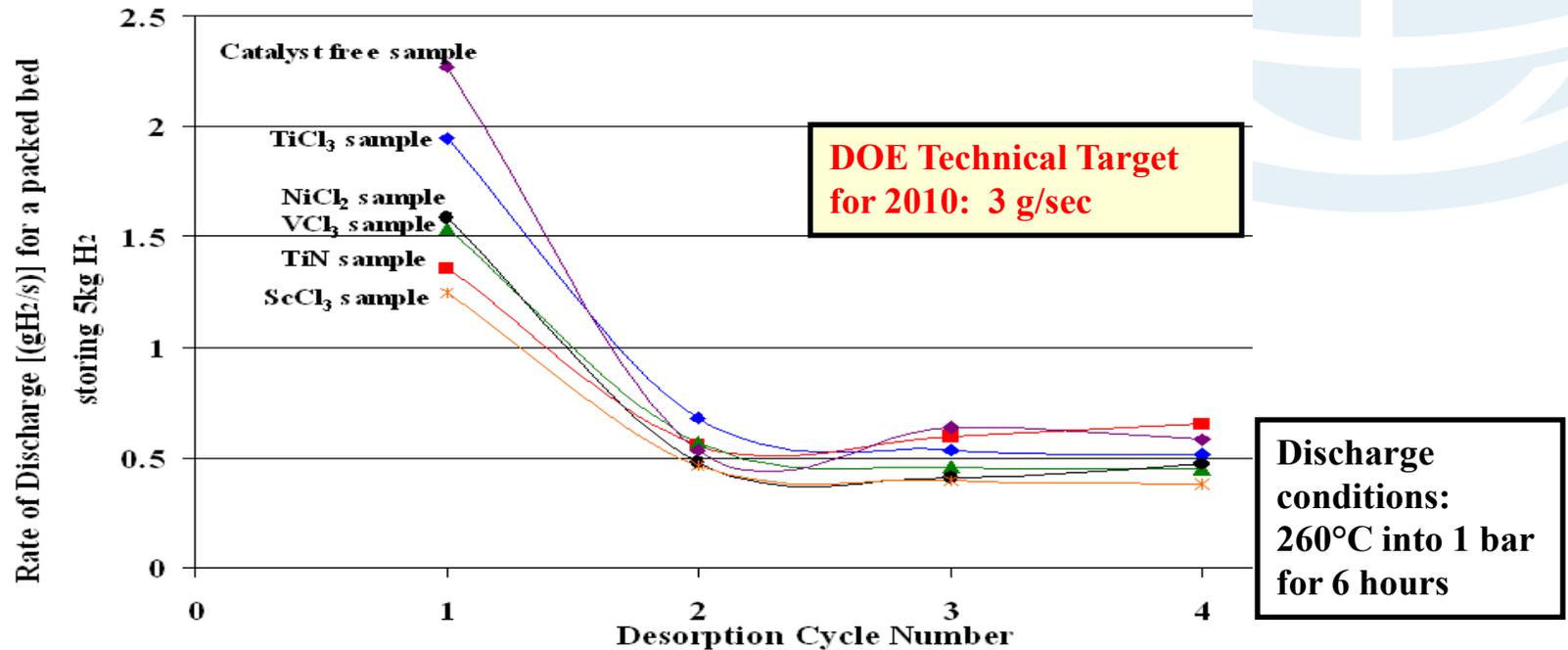
Average Rate of Hydrogen Charge for a packed bed storing 5kg H<sub>2</sub>



- Rates of hydrogen charge are an order of magnitude lower than the DoE technical target
- TiN continues to significantly increase absorption capacity through four cycles while the halide catalysts continue to decrease
  - Metathesis reaction between LiNH<sub>2</sub> and M<sub>tr</sub>Cl<sub>3</sub> hinders hydrogen absorption through the loss of essential nitrogen

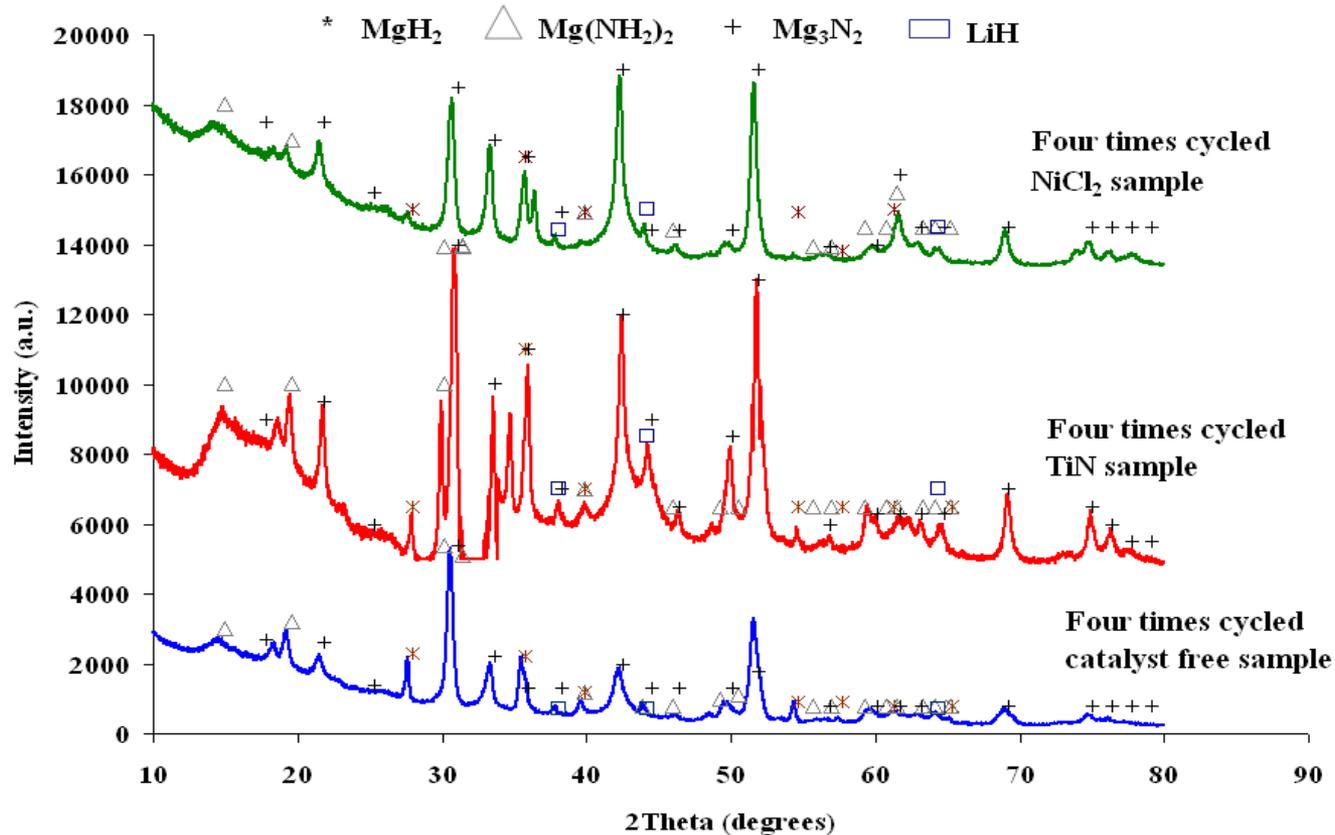
# Technical Accomplishments and Progress – Average Rate of Hydrogen Discharge [gH<sub>2</sub>/s]

Average Rate of Hydrogen Discharge for a packed bed storing 5kg H<sub>2</sub>



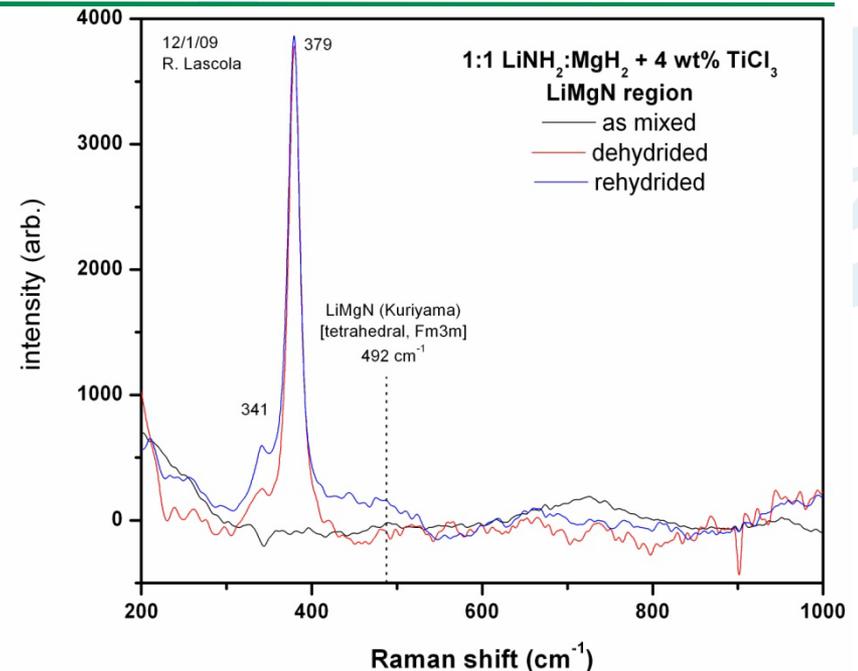
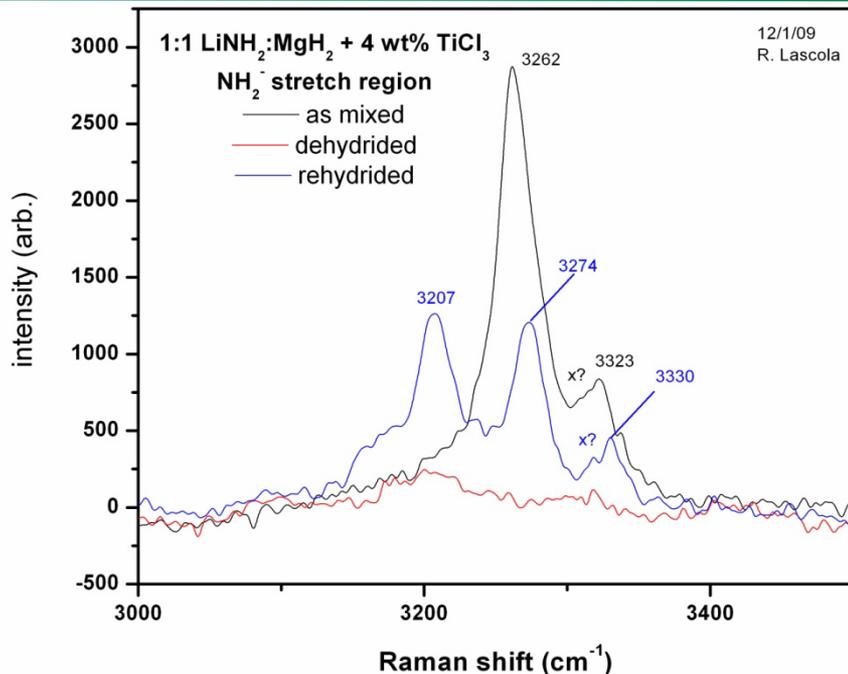
- Hydrogen discharge rate for TiN continues to increase through four cycles due to:
  - The cycled material not being completely homogenized after four cycles resulting in the loss of available surface area for the reaction to occur
- The hydrogen discharge rate decreased drastically for the halide catalysts after the first cycled due to
  - Metathesis reaction between LiNH<sub>2</sub> and M<sub>tr</sub>Cl<sub>3</sub>:  $\text{LiNH}_2 + \text{TiCl}_3 \rightarrow \text{LiCl} + \text{Ti}(\text{unknown state}) + \text{NH}_2$

# Technical Accomplishments and Progress – XRD Analysis of four cycled 1:1 LiNH<sub>2</sub>:MgH<sub>2</sub> <sup>w/w/o</sup> catalyst



- Mg(NH<sub>2</sub>)<sub>2</sub>, MgH<sub>2</sub> and LiH identified showing  $\text{LiMgN} \leftrightarrow \text{LiH} + \frac{1}{2} \text{MgH}_2 + \frac{1}{2} \text{Mg(NH}_2)_2$
- Mg<sub>3</sub>N<sub>2</sub> also identified, possibly forming from  $\text{Mg(NH}_2)_2 + 2\text{MgH}_2 \rightarrow \text{Mg}_3\text{N}_2 + 4\text{H}_2$   
 $[\Delta H = 15 \text{ kJ/mol H}_2 \text{ at } 500\text{K, Akbarzadeh, et al., Adv Mat. 19 (2007) 3233}]$  or  
 $\text{LiMgN} + \text{H}_2 \rightarrow \text{LiH} + \text{Mg}_3\text{N}_2$

# Technical Accomplishments and Progress – Raman Spectroscopy Analysis



- **As-milled:** High-shift region shows spectrum consistent with  $\text{LiNH}_2$  amide stretches
- **Discharged:** Doublet at 379 (strong) and 341 (weak)  $\text{cm}^{-1}$  which closely resembles that of  $\text{Mg}_3\text{N}_2$ ;  $\text{LiMgN}$  reported in literature [Kuriyama, *et al.*, *Phys Rev B* 75 (2005) 233204] not observed due to different crystal structure
  - Kuriyama observed a cubic disordered antiferroite structure (Fm3m),
  - Instead a nitrogen-vacancy model for antibixbyite-structure ( $\text{I}2_13$ ) was observed similar to that observed by Yamane, *et al.*, *J of Alloys and Comp* 319 (2009) 124
- **Recharged:** The bands at 3274 and 3330  $\text{cm}^{-1}$  are consistent with the formation of  $\text{Mg}(\text{NH}_2)_2$

# Conclusions for Task I - LiMgN

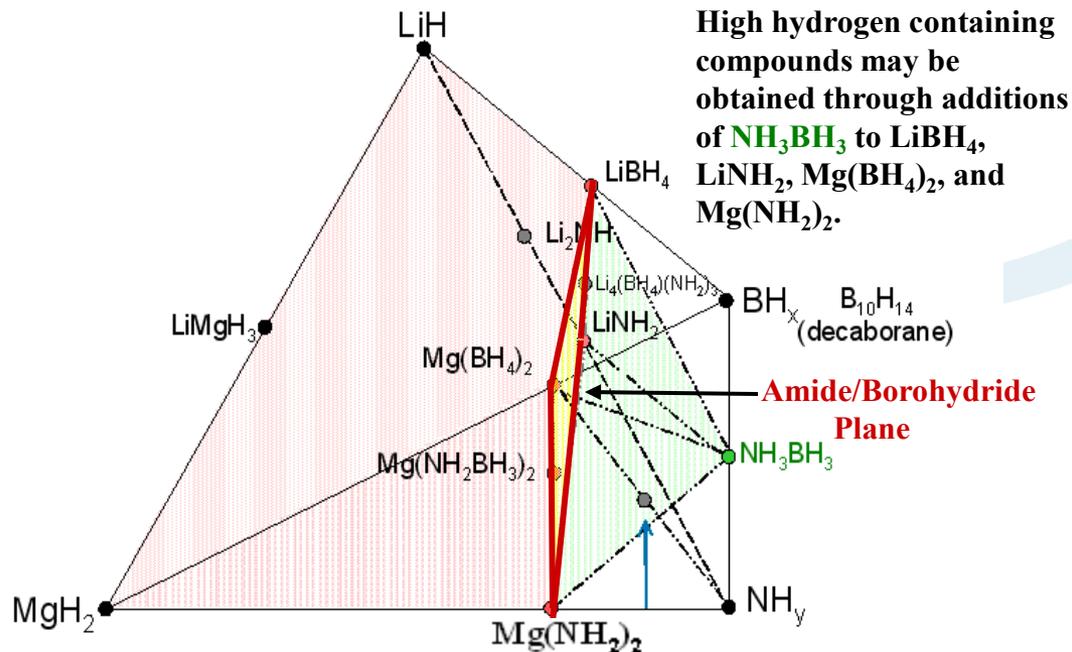
- **Catalyst composition has a significant effect on H<sub>2</sub> and NH<sub>3</sub> discharge temperatures, cyclic capacity and sorption rates**
  - **Uncatalyzed**
    - Showed a decrease in hydrogen discharge rate over four desorption cycles
      - Rate of conversion from  $\text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} > \text{LiH} + \frac{1}{2} \text{MgH}_2 + \frac{1}{2} \text{Mg}(\text{NH}_2)_2 \rightarrow \text{LiMgN}$
  - **TiN**
    - Only catalyst to increase temperature of ammonia release
    - Showed a significant increase in hydrogen capacity and rate over four absorption cycles
    - Showed an increase in hydrogen discharge rate over four desorption cycles
      - Indicates cycled material not being completely homogenized after four cycles resulting in the loss of available surface area for the reaction to occur
  - **Other catalyst**
    - Reduced the temperature of ammonia release
    - Showed decrease in sorption rates and absorption capacities over four cycles due to metathesis reaction between  $\text{LiNH}_2$  and  $\text{M}_{\text{tr}}\text{Cl}_3$
- **Sorption rates are an order of magnitude less than the 2010 DOE goals.**

# Relevance –

## Introduction of Mixed Borohydride/Amide Systems

- New set of binary anion complex compounds  $M(\text{BH}_4)_x(\text{NH}_2)_y$  exists with high wt%  $\text{H}_2$
- Relatively unexplored area with good potential for low temperature high capacity media
- The addition of mixed metal cations to the borohydride/amide compounds may decrease the strength of the B-H and N-H bonds as compared to their parent  $M(\text{BH}_4)$  chemical compounds leading to the possibility of

- amorphous compounds with significantly reduced entropy associated with dehydrogenation reaction
- provide lower heats of reaction for hydrogenation



**Ammoniation  
High Pressure  
Reactor Set-up**

## Competing Systems of Mixed Amide/Borohydride

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### Di-Anionic Complexes: $M(\text{BH}_4)^-(\text{NH}_2)^-$

- Synthesis of  $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$  and desorption  $>10\text{wt}\%$   $\text{H}_2$  at 250-350 °C, *Pinkerton et al., 2006*
- Synthesis of new  $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$  [ $\text{Li}_4\text{BN}_3\text{H}_{10}$ ], by mechano-chemical milling of  $\text{LiNH}_2$  and  $\text{LiBH}_4$ , *Chater et al., 2006*
- Theoretical calculations revealed that  $\text{Li}_4\text{BN}_3\text{H}_{10} \rightarrow \text{Li}_3\text{BN}_2 + \text{LiNH}_2 + \text{H}_2$  is only weakly endothermic, with a  $\Delta H \sim 13$  kJ/mol  $\text{H}_2$ , *Siegel et al., 2007*
- Evidence of B-H and N-H bond destabilization as compared to the parent  $\text{LiBH}_4$  and  $\text{LiNH}_2$  structures, *Yang et al., 2007*
- Impact of Stoichiometry on Hydrogen Storage Properties of  $\text{LiNH}_2 + \text{LiBH}_4 + \text{MgH}_2$  Composites, *Sudik et al., 2009* (Optimal Ratio 3:1:1.5 for  $\text{H}_2$  Desorption and Reversible at Ratio 2:1:1 and 2:0.5:1)

### Ammoniated Borohydride Complexes: $M(\text{BH}_4) \cdot \text{NH}_3$

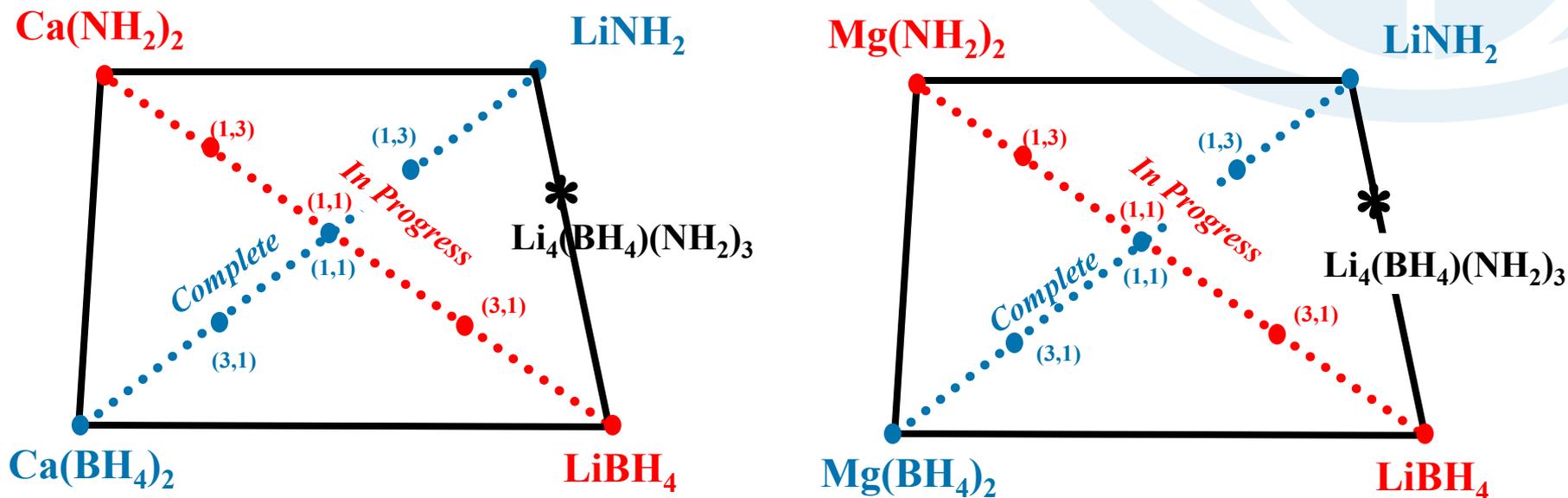
- Ammonia complex of magnesium borohydride, *Soloveichik et al., 2008*

### Amidoborane Complexes: $M(\text{NH}_2) \cdot \text{BH}_3$

- Calcium amidotrihydroborate as hydrogen storage material, *Burrell et al., 2007*

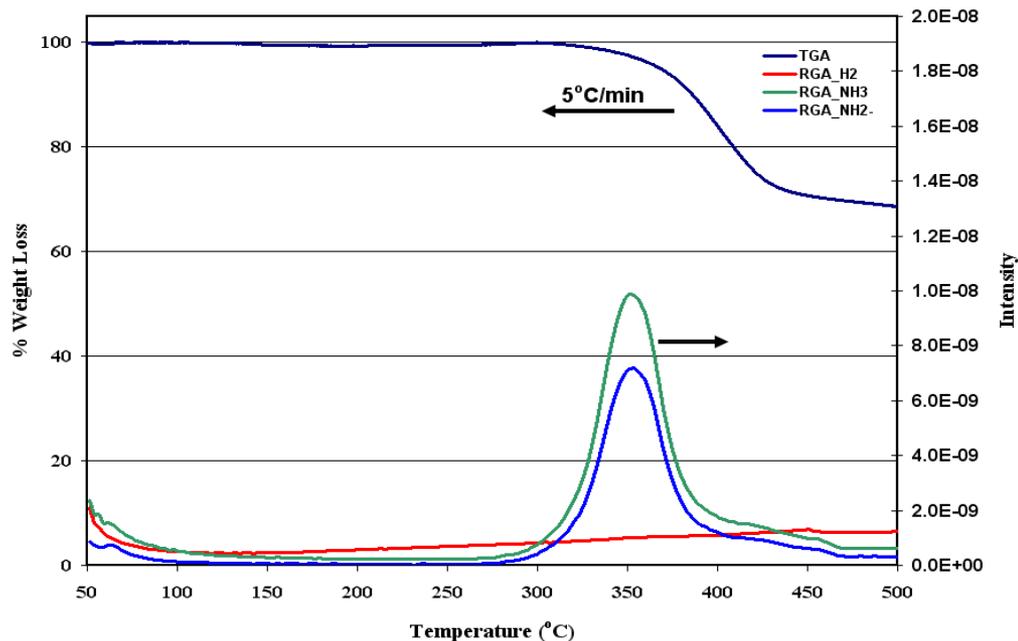
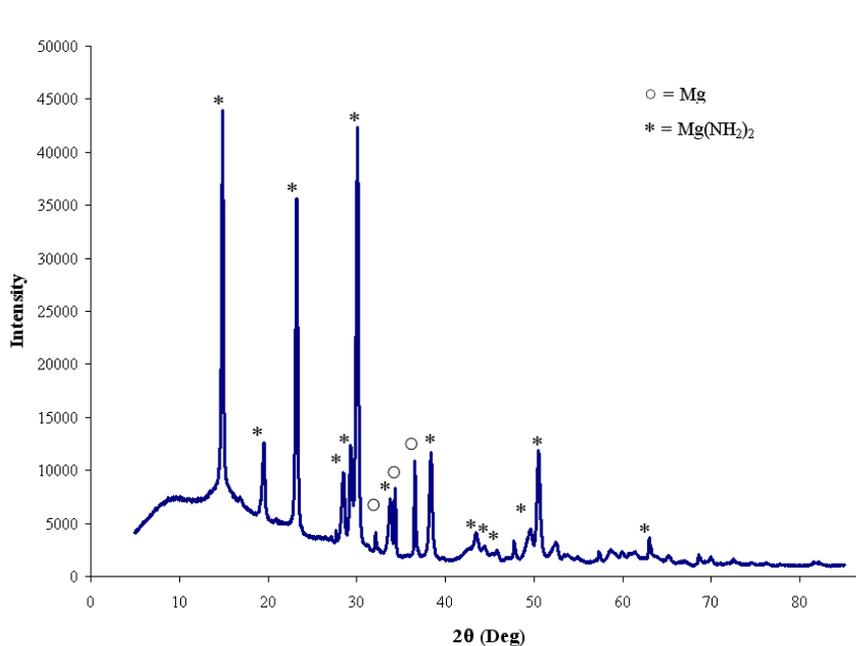
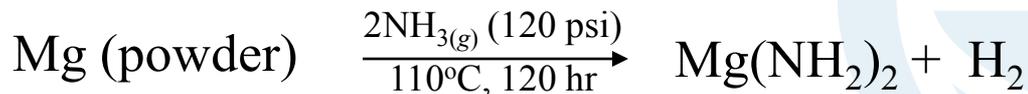
# Approach – Experimental Plan

## Amide/Borohydride Plane of Quaternary Phase Diagram



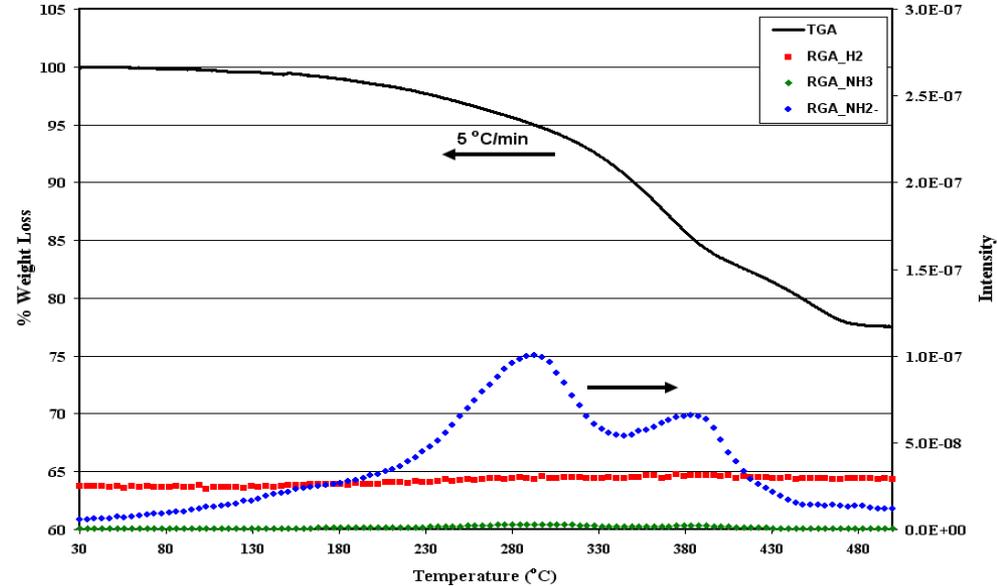
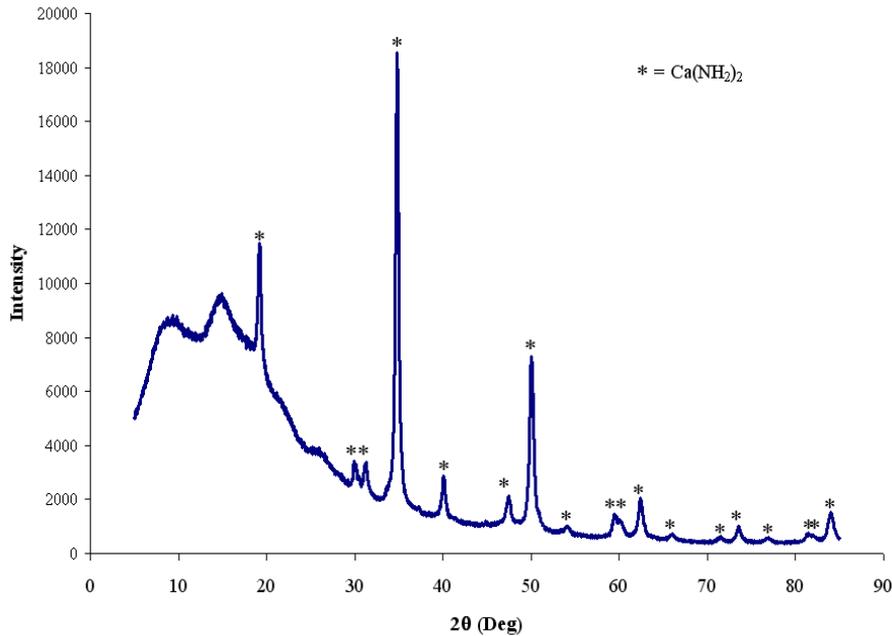
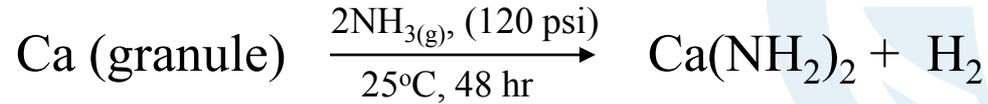
- Mixtures are formed using planetary ball-milling techniques.
- Identify isothermal/isobaric sorption properties of mixed phases using Sievert's apparatus.
- XRD analysis after ball milling process and after hydrogenation and dehydrogenation.
- TGA-RGA to determine composition of hydrogen during dehydrogenation.

# Technical Accomplishments and Progress – Synthesis of $\text{Mg}(\text{NH}_2)_2$



- XRD confirmed  $\sim 95\%$  pure  $\text{Mg}(\text{NH}_2)_2$  by simple addition of ammonia to magnesium powder and heat in a high pressure reactor vessel.
- Theoretical  $\text{H}_2$  capacity is  $\sim 7.1 \text{ wt}\%$
- TGA shows a total weight loss of more than 30%.
- RGA shows a disproportionate amount of  $\text{NH}_3$ ,  $\text{NH}_2^-$  to  $\text{H}_2$ .

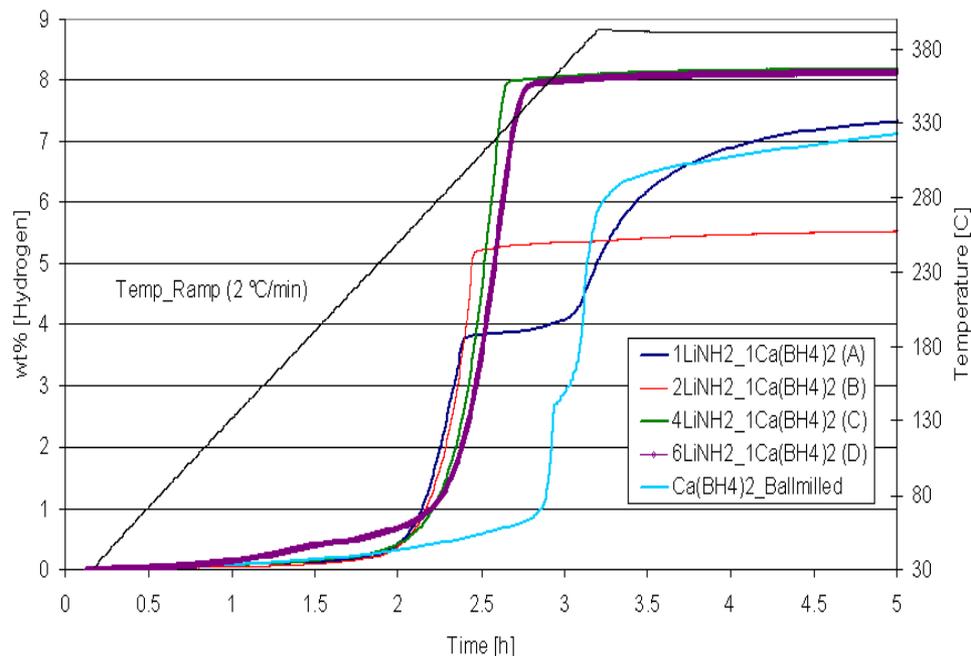
# Technical Accomplishments and Progress – Synthesis of $\text{Ca}(\text{NH}_2)_2$



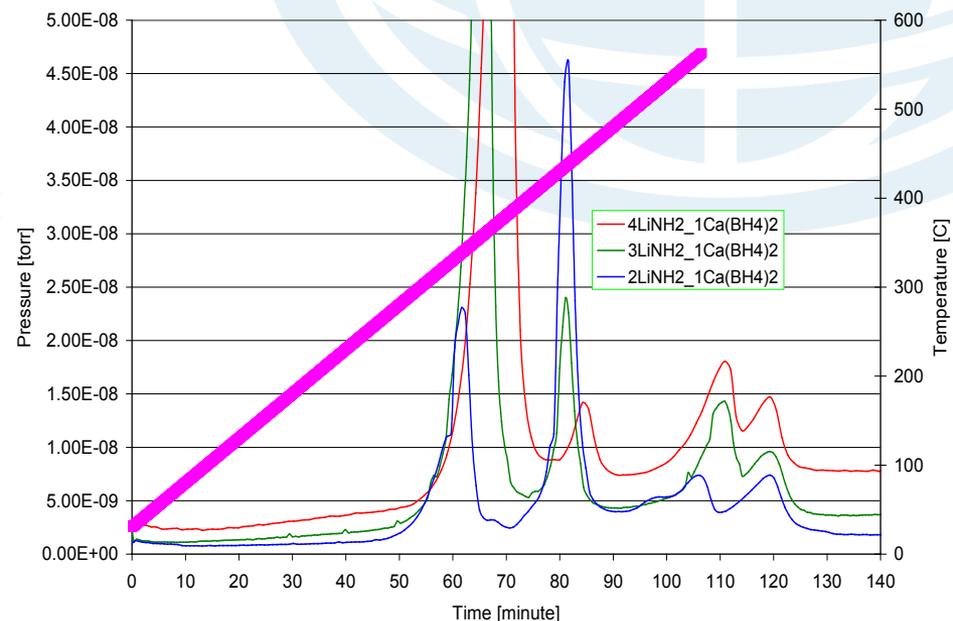
- XRD confirmed  $\sim 99\%$  pure  $\text{Ca}(\text{NH}_2)_2$  by simple addition of ammonia to calcium granules in a high pressure reactor vessel.
- Theoretical  $\text{H}_2$  capacity is  $\sim 5.5 \text{ wt}\%$
- Total weight loss from TGA is near 23%.
- RGA shows an immediate release of  $\text{NH}_2^-$  near RT followed by a release of hydrogen at around 130 $^\circ\text{C}$ , and an ammonia release at 230 $^\circ\text{C}$ .

# Technical Accomplishments and Progress – $\text{Ca}(\text{BH}_4)_2 + \text{LiNH}_2$

## Sievert's TPD:



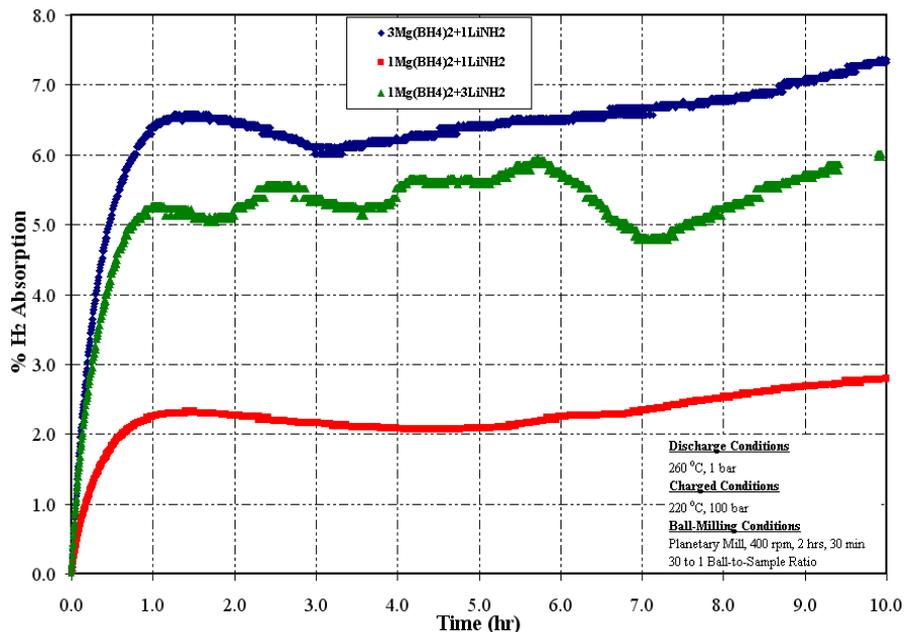
## RGA:



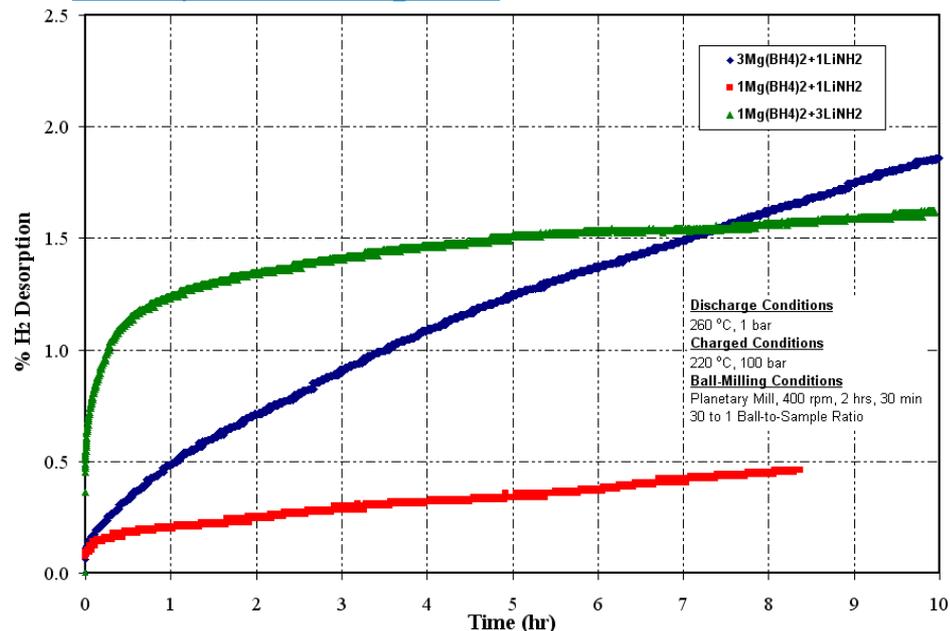
- 4 LiNH<sub>2</sub> : 1 Ca(BH<sub>4</sub>)<sub>2</sub> ratio is most effective for dehydrogenation.
- Mixtures of Ca(BH<sub>4</sub>)<sub>2</sub> and LiNH<sub>2</sub> leads to predominately H<sub>2</sub> release at 150-300°C vs NH<sub>3</sub>.
- Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> is the major phase for the 4LiNH<sub>2</sub>:1Ca(BH<sub>4</sub>)<sub>2</sub> mixture.

# Technical Accomplishments and Progress – Mg(BH<sub>4</sub>)<sub>2</sub>+LiNH<sub>2</sub>: Isothermal Sievert's Measurements

## 2<sup>nd</sup> Cycle Absorption:



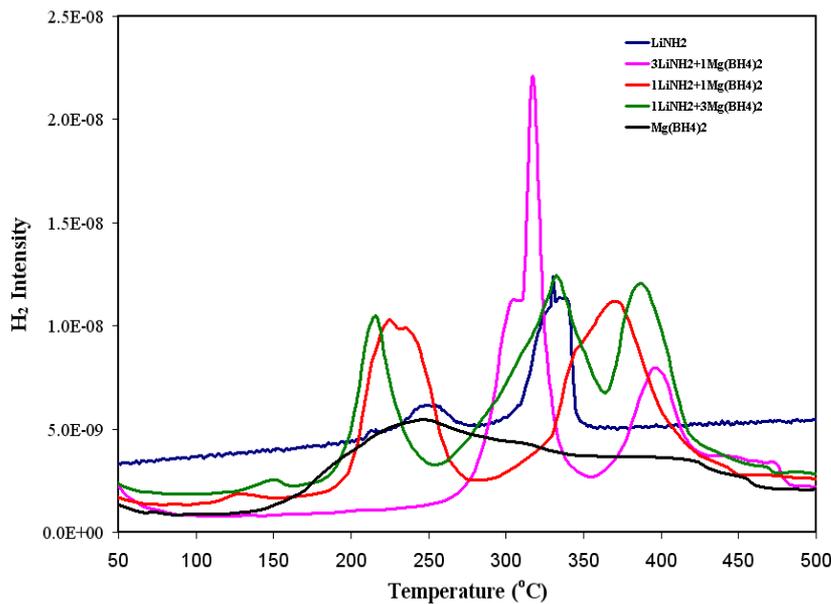
## 2<sup>nd</sup> Cycle Desorption:



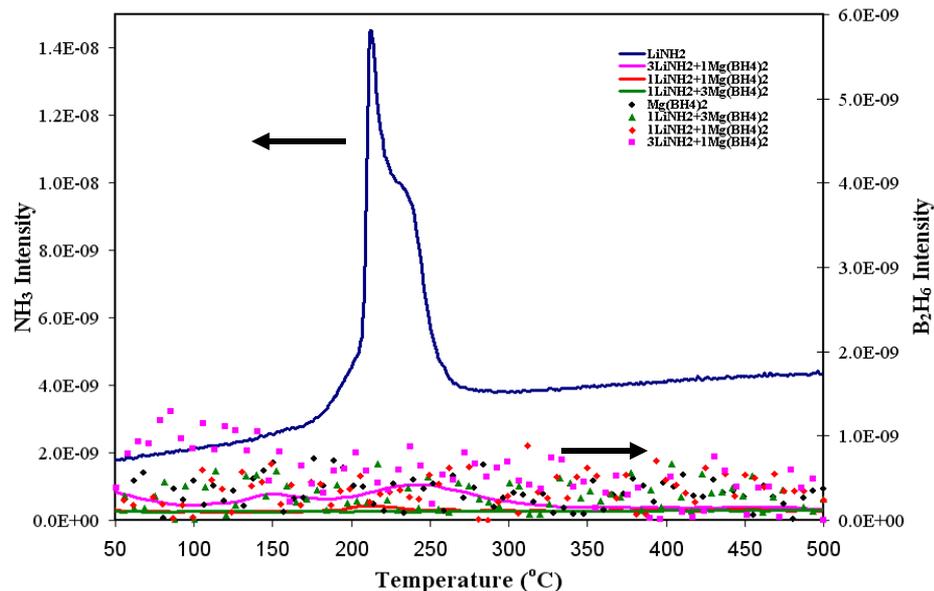
- H<sub>2</sub> absorption fluctuations occur due to competing desorption/absorption processes in the heterogeneous material.
- Absorption of the 3Mg(BH<sub>4</sub>)<sub>2</sub> + LiNH<sub>2</sub> has the maximum absorption of 7.5 wt%.
- Desorption of the 3Mg(BH<sub>4</sub>)<sub>2</sub> + LiNH<sub>2</sub> is incomplete at 2 wt% due to initial time constraints on the experiment for the mixture to reach steady state.
- Large H<sub>2</sub> absorption indicates a reversible system.

# Technical Accomplishments and Progress – Mg(BH<sub>4</sub>)<sub>2</sub>+LiNH<sub>2</sub>: RGA

## H<sub>2</sub> RGA Analysis at 5°C/min



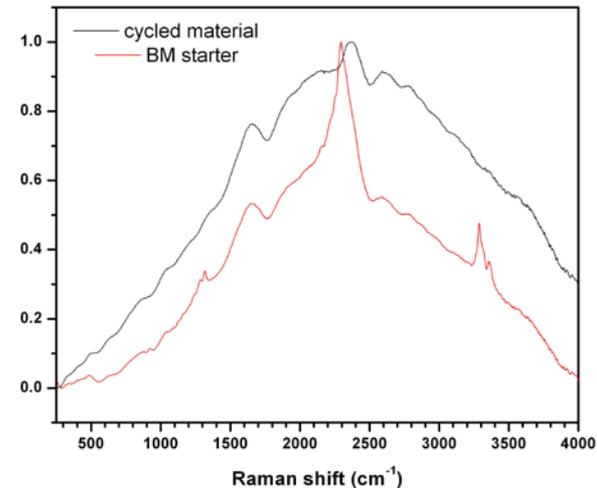
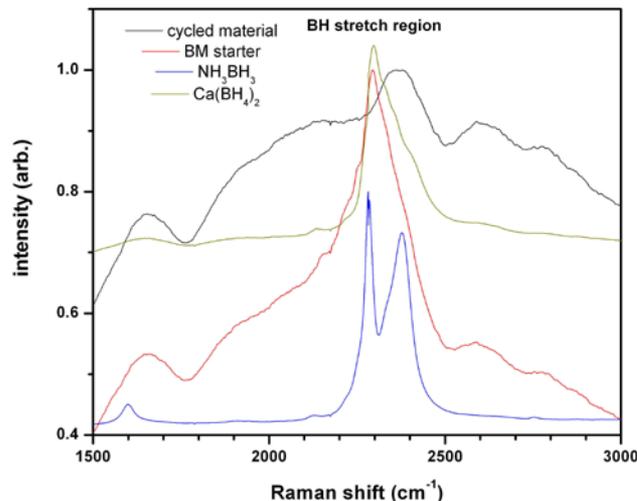
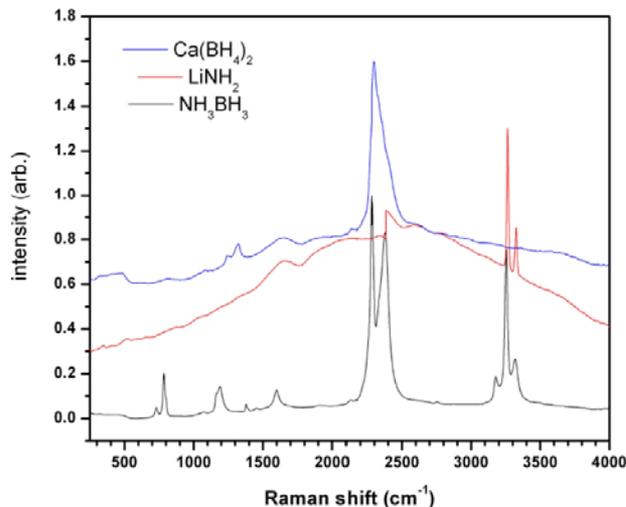
## NH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> RGA Analysis at 5°C/min



- The Mg(BH<sub>4</sub>)<sub>2</sub> and LiNH<sub>2</sub> mixtures produce multiple H<sub>2</sub> releases over the temperature range shown. Initial hydrogen release (~200°C) is at lower temperature compared to LiNH<sub>2</sub> (230°C).
- Multiple H<sub>2</sub> releases are broad which indicates more H<sub>2</sub> and less NH<sub>3</sub> (shown on the right).
- The mixtures showed a significant reduction in ammonia release compared to LiNH<sub>2</sub>. Diborane release is negligible.

# Technical Accomplishments and Progress –

## Raman Spectroscopy: $\text{Ca}(\text{BH}_4)_2 + \text{LiNH}_2 + \text{NH}_3\text{BH}_3$



\* Cycle Conditions: (d) 260°C, 1bar, 12 hr  
(c) 220°C, 100 bar, 12 hr

- spectra of the 3 starting materials look pretty much like the literature/reference spectra
- spectra of the ball-milled starting materials suggests a new material is formed:
  - BH stretch region looks a lot more like a borohydride than a borane
  - in the 1240-1350  $\text{cm}^{-1}$  region, there is an extra peak in the BM mixture compared to  $\text{Ca}(\text{BH}_4)_2$  (the peak does not appear in the spectra of the other starting materials)
- extra peaks suggest possibility of a mixed species, or a mixture of species and broadening of peaks could also be an indication of a mixture of new species

## Conclusions for Task II - $M_1M_2(BH_4)_x(NH_2)_y$

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- $Ca(NH_2)_2$  and  $Mg(NH_2)_2$  have been successfully synthesized with  $> 95\%$  purity.
- Mixtures of  $Mg(BH_4)_2$  and  $LiNH_2$  have shown good absorption capabilities but is limited kinetically on desorption through 2 cycles.
- Mixtures of  $Mg(BH_4)_2$  and  $LiNH_2$  contain multiple  $H_2$  releases, with reduced release of  $NH_3$ .
- Initial work has begun in understanding the effect of adding  $NH_3BH_3$  to  $Ca(BH_4)_2$  and  $LiNH_2$  as a potential high  $H_2$  containing mixture. Raman has confirmed that a new mixture is formed.
- Initial results show desorption of  $H_2$  as low as  $150^\circ C$  for the mixture of  $Ca(BH_4)_2:LiNH_2:NH_3BH_3$ .

# Future Directions

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- **Task I**

- Carry cycling out further than 4 complete cycles (e.g. 10 – 15 cycles for each material)
- Continue testing other catalysts to render faster kinetics and lower temperatures of operation (e.g. nano-Ti, LiBH<sub>4</sub>, KH,.....)
- Analyze the purity of the discharged H<sub>2</sub> as a function of temperature using FTIR

- **Task II**

- Complete a study of Ca(NH<sub>2</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub> ball-milled with LiBH<sub>4</sub> in various ratios.
- Continue additions of ammonia borane, decaborane and ammonia to binary compositions to evaluate possible high hydrogen compounds.
- Further investigate the sorption characteristics of the ball-milled mixtures using each mixture using Sievert's experiments.